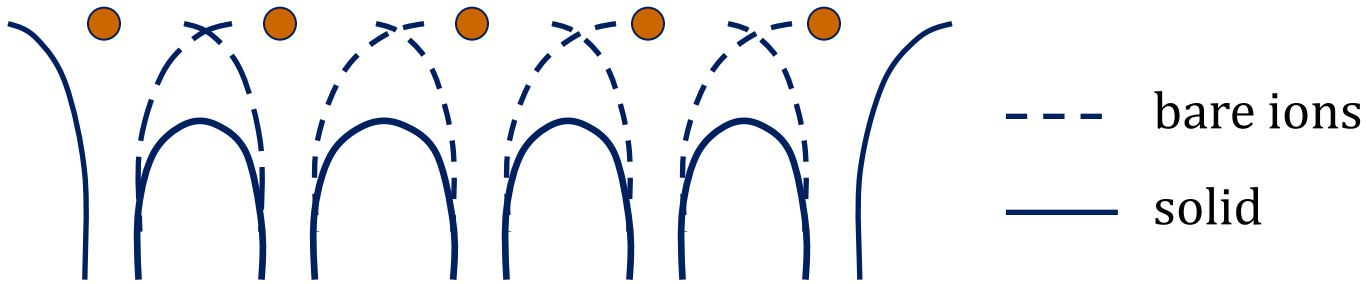
Bloch Electrons in Semiconductors

A. Band Gap
B. Equations of motion
C. Intrinsic Carrier Concentration
D. Impurity conductivity
E. Thermoelectric Effects
F. Bloch Oscillation

Energy Band Gap in a Periodic Potential

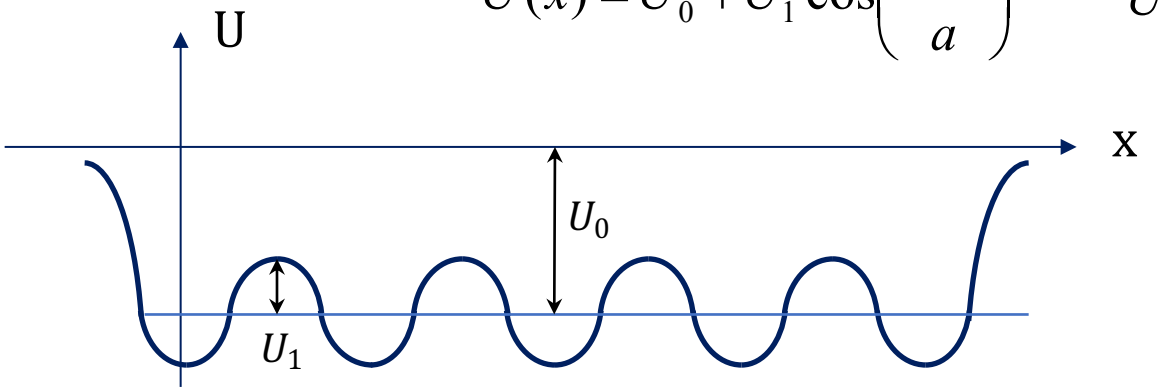
Recall the electrostatic potential energy in a crystalline solid along a line passing through a line of atoms:



Along a line parallel to this but running between atoms, the divergences of the periodic potential energy are softened.

A simple 1D model that captures the periodicity of such a potential is:

$$U(x) = U_0 + U_1 \cos\left(\frac{2\pi x}{a}\right) \qquad U_0 < U_1 < 0$$



Electron Wavefunctions in a Periodic Potential

Consider the following cases:

$U_1 = 0$ Wavefunctions are plane waves and energy bands are parabolic: $\psi = Ae^{i(kx-\omega t)}$ $E = \frac{\hbar^2 k^2}{2m}$

$U_1 \neq 0$
$k << \frac{\pi}{a}$ Electrons wavelengths much larger than a, so wavefunctions and energy bands are nearly the same as above

$U_1 \neq 0$
$k \leq \frac{\pi}{a}$ Electrons wavelengths approach a, so waves begin to be strongly back-scattered :

$$\psi_{\pm} = Ae^{i(kx-\omega t)} \pm Be^{-i(kx-\omega t)} \qquad B < A$$

$U_1 \neq 0$
$k = \frac{\pi}{a}$ Electrons waves are strongly back-scattered (Bragg scattering) so standing waves are formed:

$$\psi_{\pm} = C\left[e^{i(kx-\omega t)} \pm e^{-i(kx-\omega t)}\right] = \frac{1}{\sqrt{2}} A\left[e^{ikx} \pm e^{-ikx}\right]e^{-i\omega t}$$

Bloch Theorem and Wavefunctions

Bloch theorem is one of the most important formal results in all of solid state physics because it tells us the mathematical form of an electron wavefunction in the presence of a periodic potential energy.

In independent-electron approximation, the time-independent Schrodinger equation for an electron in a periodic potential is:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right]\psi = E\psi$$

where the potential energy is invariant under a lattice translation vector $\boldsymbol{T}$:

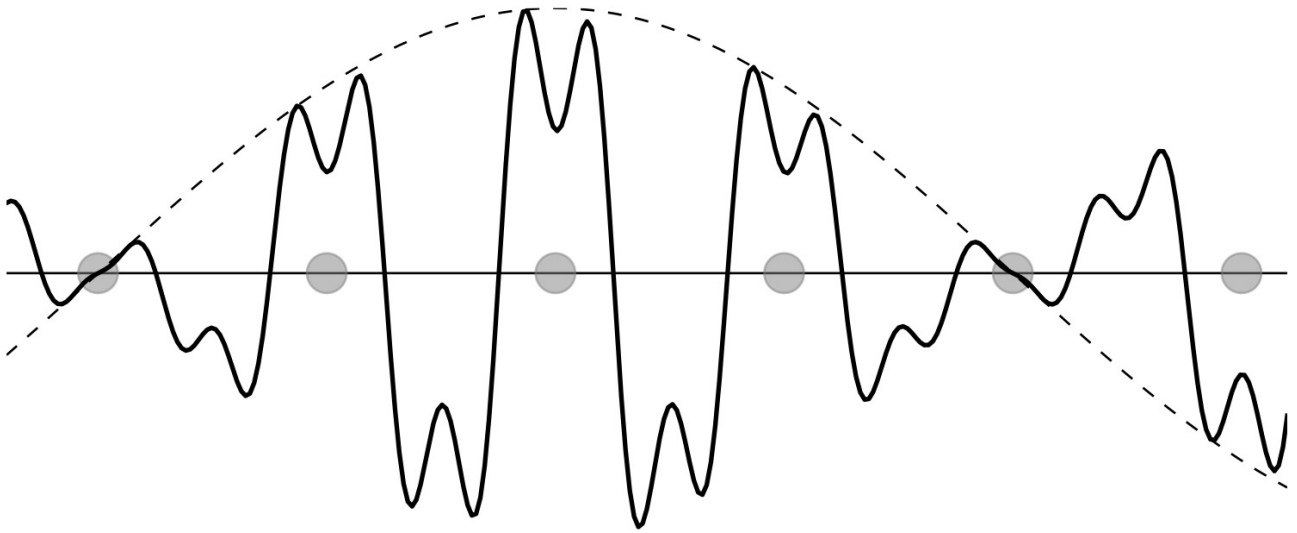
$$U(\boldsymbol{r} + \boldsymbol{T}) = U(\boldsymbol{r}) \quad \text{and} \quad \boldsymbol{T} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$$

Bloch showed that the solutions to the SE are the product of a plane wave and a function with the periodicity of the lattice:

$$\boxed{\psi_{\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{T}) = u_{\boldsymbol{k}}(\boldsymbol{r})e^{i\boldsymbol{k}\cdot\boldsymbol{r}}} \quad \text{and} \quad u_{\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{T}) = u_{\boldsymbol{k}}(\boldsymbol{r})$$

Bloch Wavefunctions

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$$



This result gives evidence to support the nearly-free electron approximation, in which the periodic potential is assumed to have a very small effect on the plane-wave character of a free electron wavefunction. It also explains why the free-electron gas model is so successful for the simple metals!

Band Gap

The **band gap** is the difference in energy between the lowest point of the conduction band and the highest point of the valence band. The lowest point in the conduction band is called the **conduction band edge**; the highest point in the valence band is called the **valence band edge**.

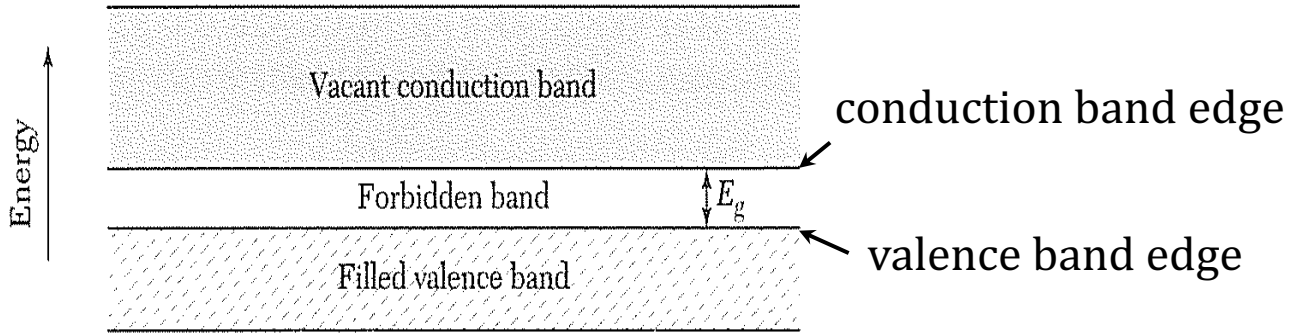
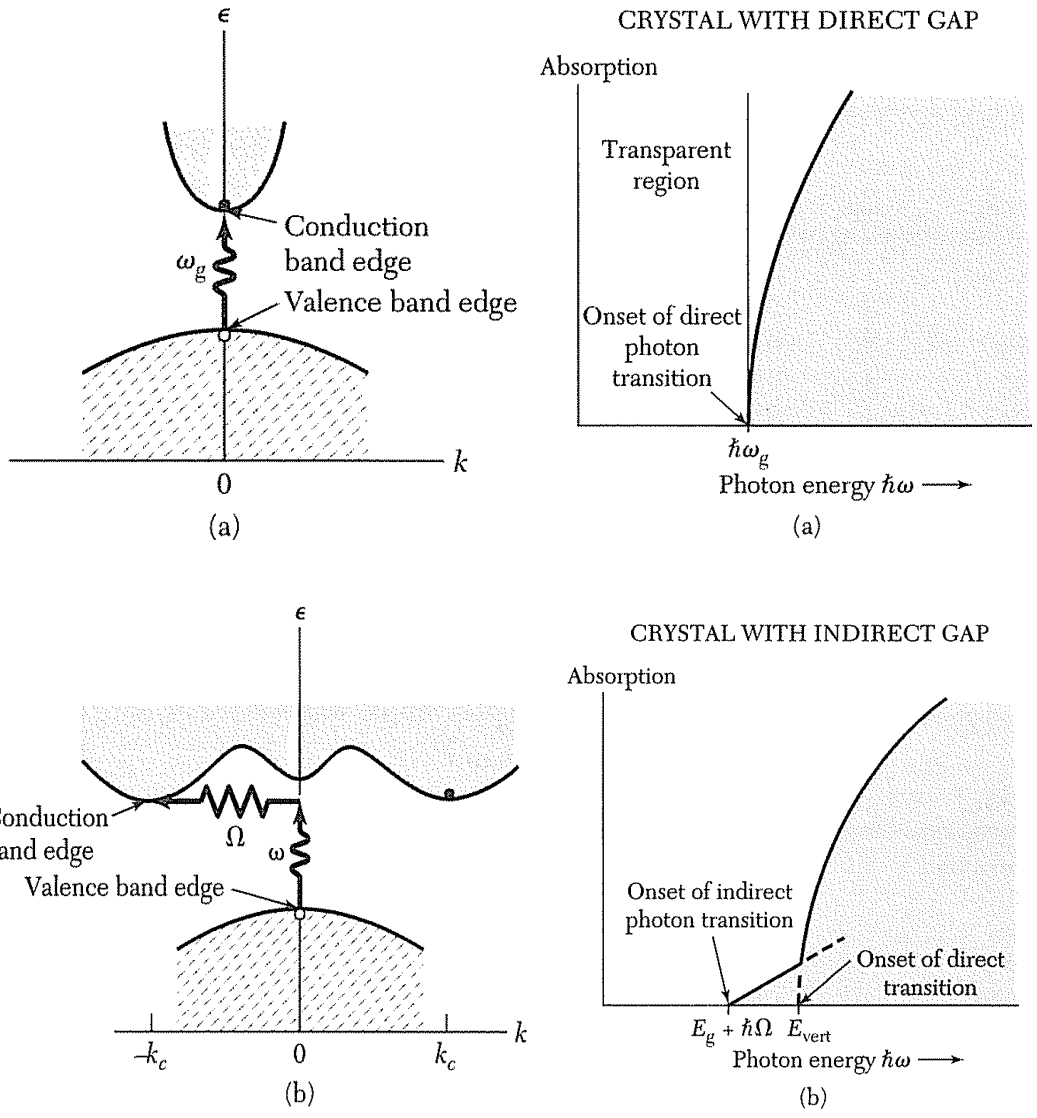


Table 1 Energy gap between the valence and conduction bands
(*i* = indirect gap; *d* = direct gap)

		E_g, eV				E_g, eV	
Crystal	Gap	0 K	300 K	Crystal	Gap	0 K	300 K
Diamond	*i*	5.4		SiC(hex)	*i*	3.0	—
Si	*i*	1.17	1.11	Tc	*d*	0.33	—
Ge	*i*	0.744	0.66	HgTe[a]	*d*	−0.30	
αSn	*d*	0.00	0.00	PbS	*d*	0.286	0.34–0.37
InSb	*d*	0.23	0.17	PbSe	*i*	0.165	0.27
InAs	*d*	0.43	0.36	PbTe	*i*	0.190	0.29
InP	*d*	1.42	1.27	CdS	*d*	2.582	2.42
GaP	*i*	2.32	2.25	CdSe	*d*	1.840	1.74
GaAs	*d*	1.52	1.43	CdTe	*d*	1.607	1.44
GaSb	*d*	0.81	0.68	SnTe	*d*	0.3	0.18
AlSb	*i*	1.65	1.6	Cu_2O	*d*	2.172	—

Direct and Indirect Band Gaps



Band gaps can be measured by optical absorption. In a direct absorption process the threshold of continuous optical absorption at ω_g measures the energy band gap $E_g = \hbar\omega_g$.

In the indirect absorption process the minimum energy gap of the band structure involves electrons and holes separated by a substantial wavevector $\mathbf{k}_c$. If a phonon of wavevector $\mathbf{K}$ and frequency Ω is created, then

$$\mathbf{k}(\text{photon}) = \mathbf{k}_c + \mathbf{K} \cong \mathbf{0} \ ;$$

$$\hbar\omega = E_g + \hbar\Omega \ ,$$

Equations of Motion

The propagation speed of an electron wavepacket in a periodic crystal can be calculated from the energy band along that direction in reciprocal space:

electron velocity: (1-D) $v_g = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{dE}{dk}$ (3-D) $\boldsymbol{v}_g(\mathbf{k}) = \hbar^{-1}\boldsymbol{\nabla}_{\mathbf{k}}\epsilon(\mathbf{k})$

The work $\delta\epsilon$ done on the electron by the electric field E in the time δt is

$$\delta\epsilon = -eEv_g\,\delta t\ , \quad \text{and since} \quad \delta\epsilon = (d\epsilon/dk)\delta k = \hbar v_g\,\delta k\ ,$$

we have $\delta k = -(eE/\hbar)\delta t$, and $\hbar dk/dt = -eE = \mathrm{F}$, so we obtain

$$\boxed{\hbar\frac{d\mathbf{k}}{dt} = \mathbf{F}\ .}$$

This is an important relation: in a crystal $\hbar d\mathbf{k}/dt$ is equal to the external force on the electron. In free space $d(m\mathbf{v})/dt$ is equal to the force. We have not overthrown Newton's second law of motion: the electron in the crystal is subject to forces from the crystal lattice as well as from external sources.

In a constant magnetic field **B**, the equation of motion is

$$\hbar\frac{d\mathbf{k}}{dt} = -\frac{e}{c}\mathbf{v}\times\mathbb{B} \quad \text{or} \quad \frac{d\mathbf{k}}{dt} = -\frac{e}{\hbar^2 c}\nabla_{\mathbf{k}}\epsilon\times\mathbb{B} \quad \text{with} \quad \mathbf{v} = \hbar^{-1}\nabla_{\mathbf{k}}\epsilon$$

an electron moves in $\mathbf{k}$ space in a direction normal to the direction of the gradient of the energy ϵ, so that **the electron moves on a surface of constant energy**. The value of the projection $k_{\mathbf{B}}$ of $\mathbf{k}$ on $\mathbb{B}$ is constant during the motion. The motion in $\mathbf{k}$ space is on a plane normal to the direction of $\mathbb{B}$, and the orbit is defined by the intersection of this plane with a surface of constant energy.

Physical Derivation of Equations of Motion

Bloch eigenfunction $\psi_{\mathbf{k}}$ belonging to the energy $\epsilon_{\mathbf{k}}$ and wavevector $\mathbf{k}$:

$$\psi_{\mathbf{k}} = \sum_{\mathbf{G}} C(\mathbf{k} + \mathbf{G}) \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}]$$

The expectation value of the momentum of an electron in the Bloch state $\mathbf{k}$ is

$$\mathbf{P}_{\text{el}} = (\mathbf{k}|-i\hbar\nabla|\mathbf{k}) = \sum_{\mathbf{G}} \hbar(\mathbf{k} + \mathbf{G})|C(\mathbf{k} + \mathbf{G})|^2 = \hbar(\mathbf{k} + \sum_{\mathbf{G}} \mathbf{G}|C(\mathbf{k} + \mathbf{G})|^2) \ ,$$

We suppose that a weak external force is applied to the crystal in a time interval such that the total impulse is $\mathbf{J} = \int \mathbf{F}\, dt$. We will have

$$\mathbf{J} = \Delta\mathbf{p}_{\text{tot}} = \Delta\mathbf{p}_{\text{lat}} + \Delta\mathbf{p}_{\text{el}}$$

The change of momentum of the electron will be

$$\Delta \mathbf{p}_{\text{el}} = \hbar \Delta \mathbf{k} + \sum_{\mathbf{G}} \hbar \mathbf{G} [(\nabla_{\mathbf{k}} |C(\mathbf{k} + \mathbf{G})|^2) \cdot \Delta \mathbf{k}]$$

The change $\Delta \mathbf{p}_{\text{lat}}$ in the lattice momentum resulting from the change of state of the electron is

$$\Delta \mathbf{p}_{\text{lat}} = -\hbar \sum_{\mathbf{G}} \mathbf{G} [(\nabla_{\mathbf{k}} |C(\mathbf{k} + \mathbf{G})|^2 \cdot \Delta \mathbf{k}]$$

The total momentum change is therefore

$$\Delta \mathbf{p}_{\text{el}} + \Delta \mathbf{p}_{\text{lat}} = \mathbf{J} = \hbar \Delta \mathbf{k}$$

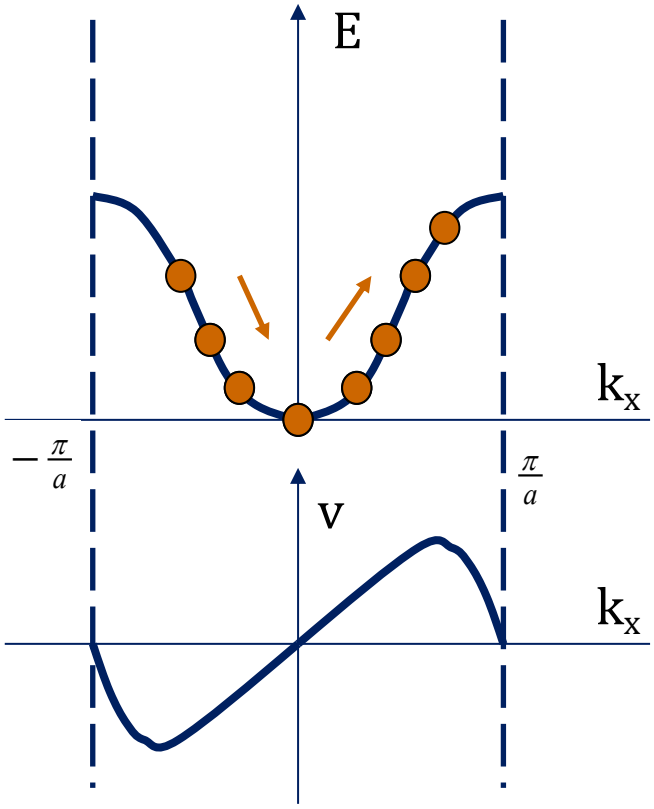
Since $d\mathbf{J}/dt = \mathbf{F}$, we thus have

$$\boxed{\hbar d\mathbf{k}/dt = \mathbf{F}}$$

Band Electron in E Field

Now we see that the external electric field causes a change in the k vectors of all electrons:

$$\vec{F} = \hbar \frac{d\vec{k}}{dt} = -e\vec{E} \longrightarrow \frac{d\vec{k}}{dt} = \frac{-e\vec{E}}{\hbar}$$



If the electrons are in a partially filled band, this will break the symmetry of electron states in the 1st BZ and produce a net current. But if they are in a filled band, even though all electrons change k vectors, the symmetry remains, so J = 0.

When an electron reaches the 1st BZ edge (at $k = \pi/a$) it immediately reappears at the opposite edge ($k = -\pi/a$) and continues to increase its k .

As an electron's k value increases, its velocity increases, then decreases to zero and then becomes negative when it reemerges at $k = -\pi/a$.

Thus, an AC current is predicted to result from a DC field (Bloch oscillations).

Properties of Holes

Holes are vacant orbits in a band whose properties are important in an almost filled band.

A hole acts in applied electric and magnetic fields as if it has a positive charge $+e$. The reason is given in five steps that follow:

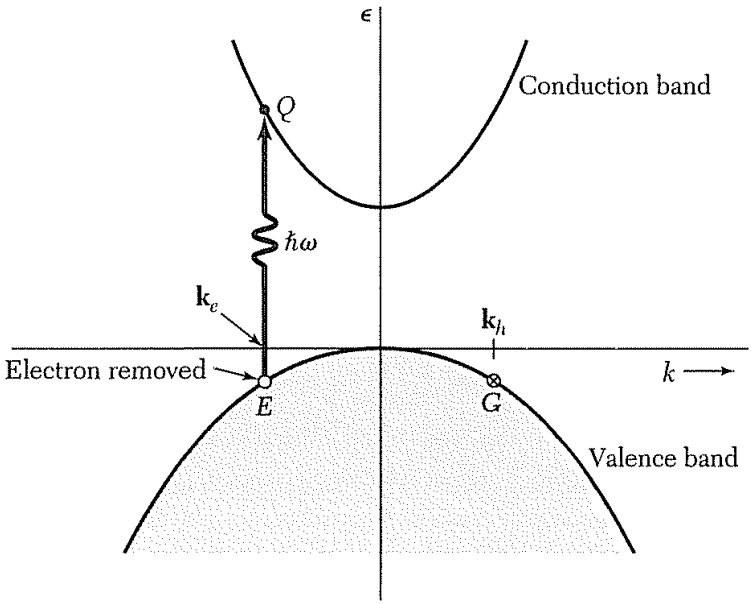
1. Crystal momentum: $\mathbf{k}_h = -\mathbf{k}_e$

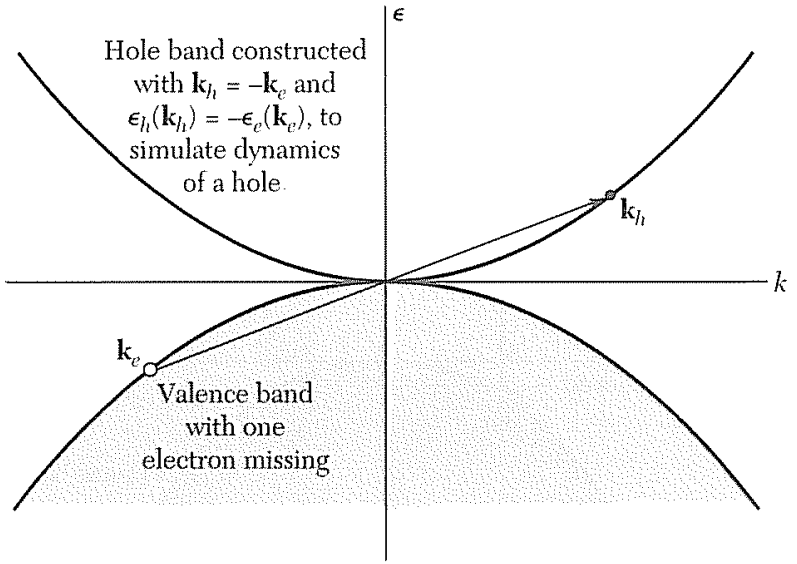
The total wavevector of the electrons in a filled band is zero: $\Sigma\mathbf{k} = 0$, where the sum is over all states in a Brillouin zone. This result follows from the geometrical symmetry of the Brillouin zone: every fundamental lattice type has symmetry under the inversion operation $\mathbf{r} \rightarrow -\mathbf{r}$

If an electron is missing from an orbital of wavevector $\mathbf{k}_e$, the total wavevector of the system is $-\mathbf{k}_e$ and is attributed to the hole.

2. Energy: $\epsilon_h(\mathbf{k}_h) = -\epsilon_e(\mathbf{k}_e)$

The energy of the hole is opposite in sign to the energy of the missing electron, because it takes more work to remove an electron from a low orbital than from a high orbital.





3. Velocity: $\mathbf{v}_h = \mathbf{v}_e$

The velocity of the hole is equal to the velocity of the missing electron.

Since $\nabla\epsilon_h(\boldsymbol{k}_h) = \nabla\epsilon_e(\boldsymbol{k}_e)$, so that $\boldsymbol{v}_h(\boldsymbol{k}_h) = \boldsymbol{v}_e(\boldsymbol{k}_e)$.

4. Effective mass: $m_h = -m_e$

The effective mass is inversely proportional to the curvature $d^2\epsilon/dk^2$.

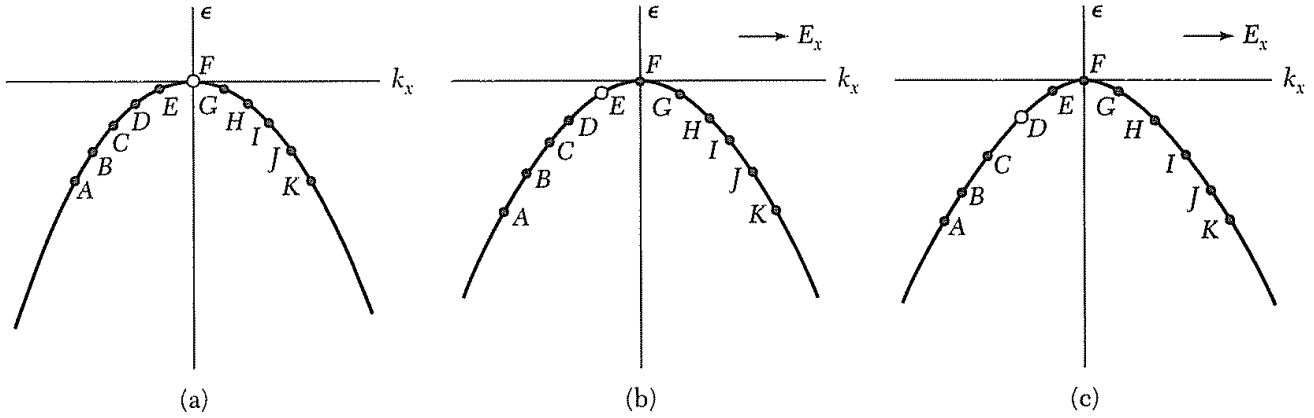
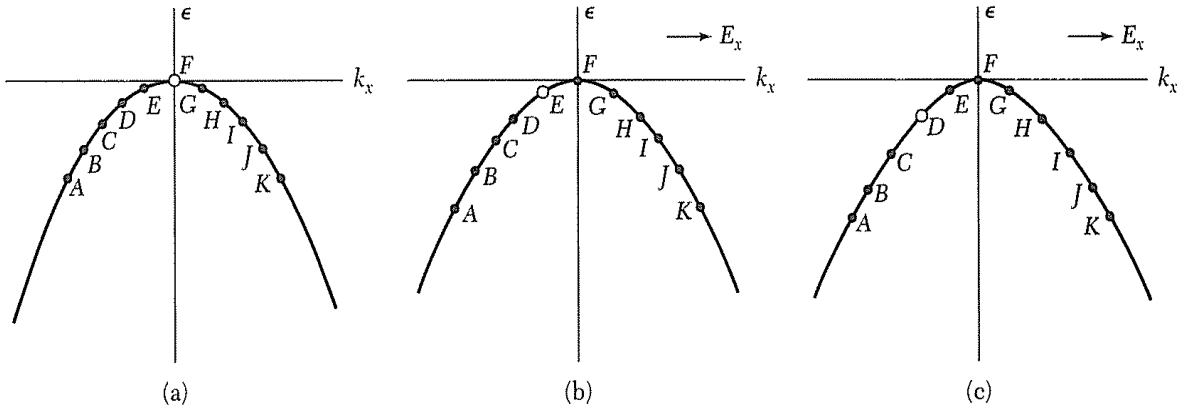


Figure 9 (a) At $t = 0$ all states are filled except F at the top of the band; the velocity v_x is zero at F because $d\epsilon/dk_x = 0$. (b) An electric field E_x is applied in the $+x$ direction. The force on the electrons is in the $-k_x$ direction and all electrons make transitions together in the $-k_x$ direction, moving the hole to the state E. (c) After a further interval the electrons move farther along in k space and the hole is now at D.

5. Equation of motion: $$\hbar \frac{d\mathbf{k}_h}{dt} = e(\mathbf{E} + \frac{1}{c}\mathbf{v}_h \times \mathbf{B})$$

The equation of motion for a hole is that of a particle of positive charge *e*.



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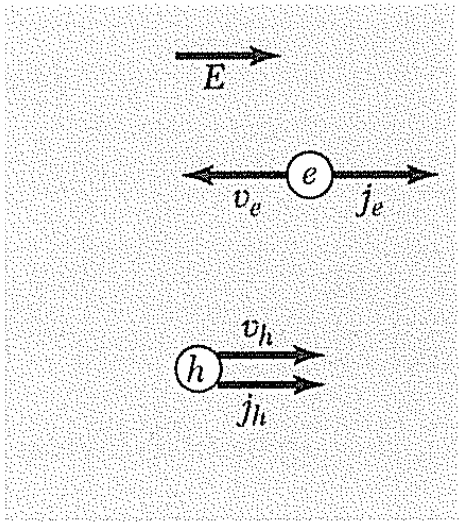


Electrons and Holes

A full band can be written as: $\sum_{i\neq+j}^{\pm N/2} \vec{k}_i + \vec{k}_j = 0$ and $\sum_{i\neq+j}^{\pm N/2} \vec{k}_i = -\vec{k}_j = \vec{k}_{-j}$

So when the state +j is empty in a band, the band has effective wavevector k_{-j}.

Now the current flow in the incomplete band under the influence of a field E:

$$\sum_{i=\pm1}^{\pm N/2} \left(-e\vec{v}_i\right) = \underbrace{\sum_{i\neq+j}^{\pm N/2} \left(-e\vec{v}_i\right)}_{e\vec{v}_j} - e\vec{v}_j = 0$$

This shows that an incomplete band (state +j empty) behaves just like a positive charge moving with the same velocity an electron would have in that state.

Thus the properties of all of the remaining electrons in the incomplete band are equivalent to those of the vacant state j if the vacant state has:

a. A k-vector k_{-j}
b. A velocity v_{+j}
c. A positive charge $+e$

We call this vacant state a positive "hole" (h^+)

Dynamics of Electrons and Holes

If this hole is accelerated in an applied electric field: $m_h \frac{d\vec{v}_h}{dt} = +e\vec{E}$

The corresponding equation for the electron is: $m_e \frac{d\vec{v}_e}{dt} = -e\vec{E}$

But earlier we deduced that the hole velocity is the same as that of the corresponding "missing" electron: $\vec{v}_h = \vec{v}_e$

So by equating the derivatives we find: $\frac{e\vec{E}}{m_h} = -\frac{e\vec{E}}{m_e} \longrightarrow m_h = -m_e$

However, note that near the top of a band the band curvature is negative, so the effective electron mass is also negative. The corresponding hole mass is then positive.

So the equation of motion of a "hole" in an electromagnetic field is:

$$\vec{F} = \hbar \frac{d\vec{k}_h}{dt} = e\left(\vec{E} + \vec{v}_h \times \vec{B}\right)$$

This explains why some metals have positive R_H.

Band Effective Mass of an Electron

We can write the equation of motion of a Bloch electron in 1-D:

$$a_x = \frac{dv_x}{dt} = \frac{dv_x}{dk_x}\frac{dk_x}{dt} \qquad \text{and} \qquad \frac{dv_x}{dk_x} = \frac{dv_g}{dk_x} = \frac{d}{dk_x}\left(\frac{1}{\hbar}\frac{dE}{dk_x}\right) = \frac{1}{\hbar}\frac{d^2E}{dk_x^2}$$

Also, from the acceleration theorem: $\frac{dk_x}{dt} = \frac{F_x}{\hbar}$

This gives:

$$a_x = \frac{1}{\hbar}\frac{d^2E}{dk_x^2}\left(\frac{F_x}{\hbar}\right) \qquad \text{or} \qquad F_x = \frac{\hbar^2}{\dfrac{d^2E}{dk_x^2}}a_x$$

With the analogy of F = *ma*, the band effective mass is defined as:

$$m^* \equiv \frac{\hbar^2}{\dfrac{d^2E}{dk_x^2}} \qquad \text{or} \qquad \boxed{\frac{1}{m^*} \equiv \frac{1}{\hbar^2}\frac{d^2E}{dk_x^2}}$$

The effective mass depends on the electron's energy and thus its location in the band.

Physical Meaning of Effective Mass

For a free electron:

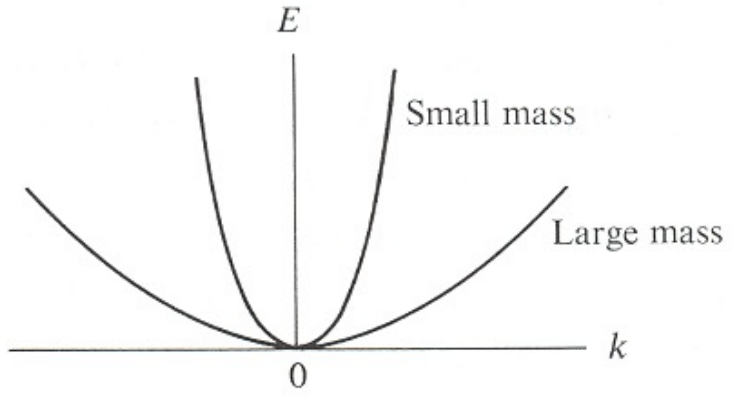
$$E = \frac{\hbar^2 k_x^2}{2m} \qquad \text{and} \qquad m^* \equiv \frac{\hbar^2}{\left(\frac{\hbar^2}{m}\right)} = m$$

In a 3-D solid we would find that m* is a second-order tensor with 9 components:

$$\frac{1}{m^*} \equiv \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_i \partial k_j} \qquad i, j = x, y, z$$

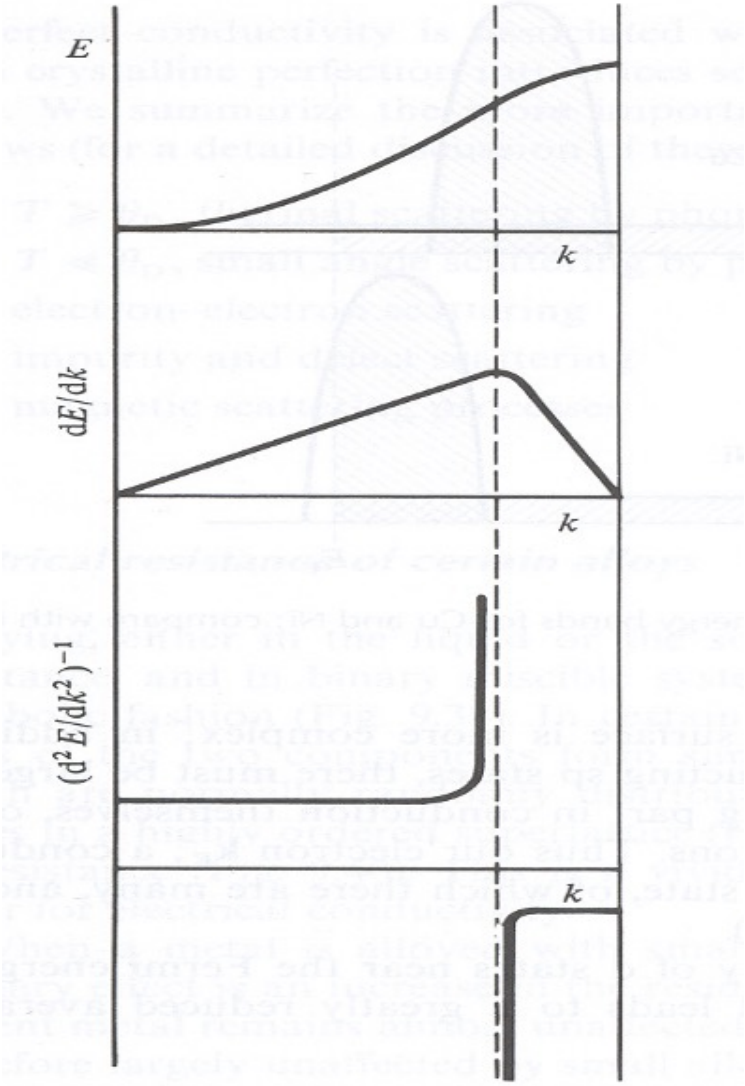
The effective mass concept if useful because it allows us to retain the notion of a free-electron even when we have a periodic potential, as long as we use m* to account for the effect of the lattice on the acceleration of the electron.

Physical Meaning of Effective Mass



The effective mass is inversely proportional to the curvature of the energy band.

Near the bottom of a nearly-free electron band m* is approximately constant, but it increases dramatically near the inflection point and even becomes negative near the zone edge.



Metals, Insulators, and Semiconductors

For reasons that will be explained more fully later:

- Metals are solids with incompletely filled energy bands
- Semiconductors and insulators have a completely filled or empty bands and an energy gap separating the highest filled and lowest unfilled band. Semiconductors have a small energy gap ($E_g < 2.0$ eV).

Quick quiz: Does this mean a divalent element will always be an insulator?

Answer: In 1-D, yes, but not necessarily in 2-D or 3-D! Bands along different directions in k-space can overlap, so that electrons can partially occupy both of the overlapping bands and thus form a metal.

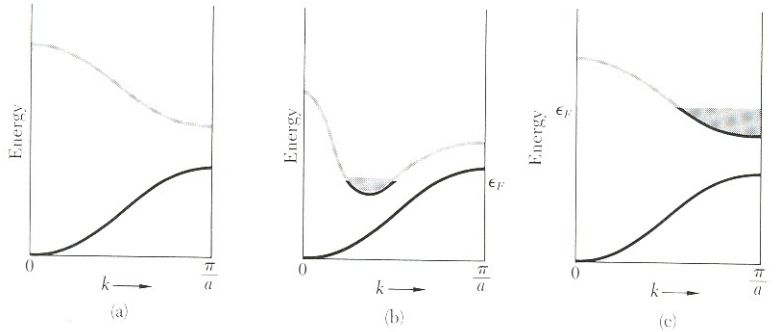
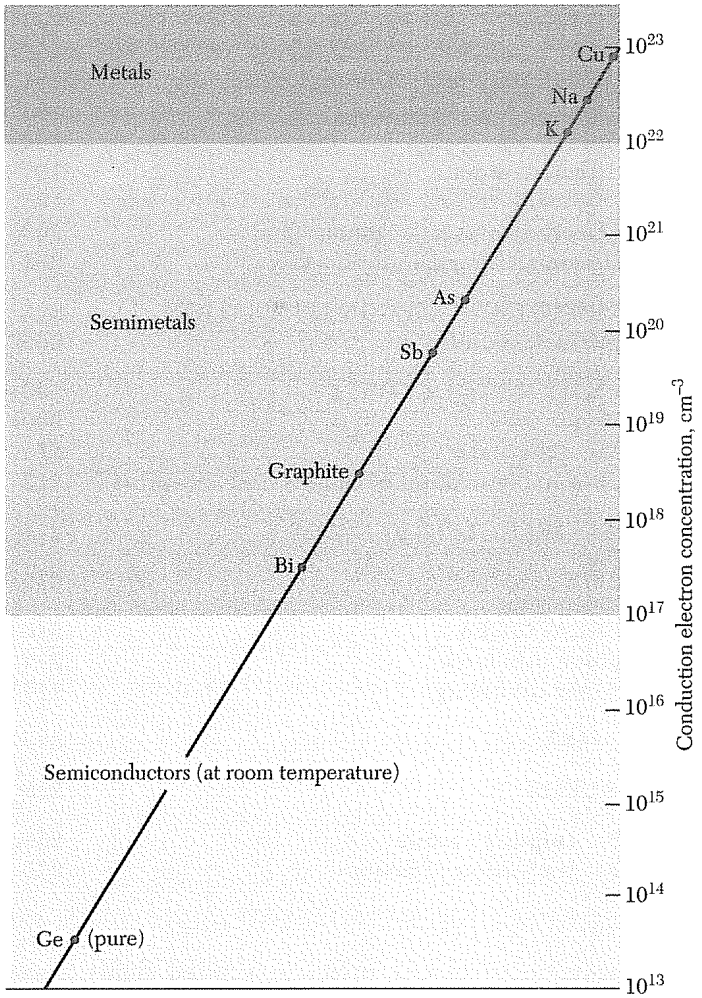


Figure 11 Occupied states and band structures giving (a) an insulator, (b) a metal or a semimetal because of band overlap, and (c) a metal because of electron concentration. In (b) the overlap need not occur along the same directions in the Brillouin zone. If the overlap is small, with relatively few states involved, we speak of a semimetal.

But it is true that only crystals with an even number of valence electrons in a primitive cell can be insulators.

Carrier Concentrations

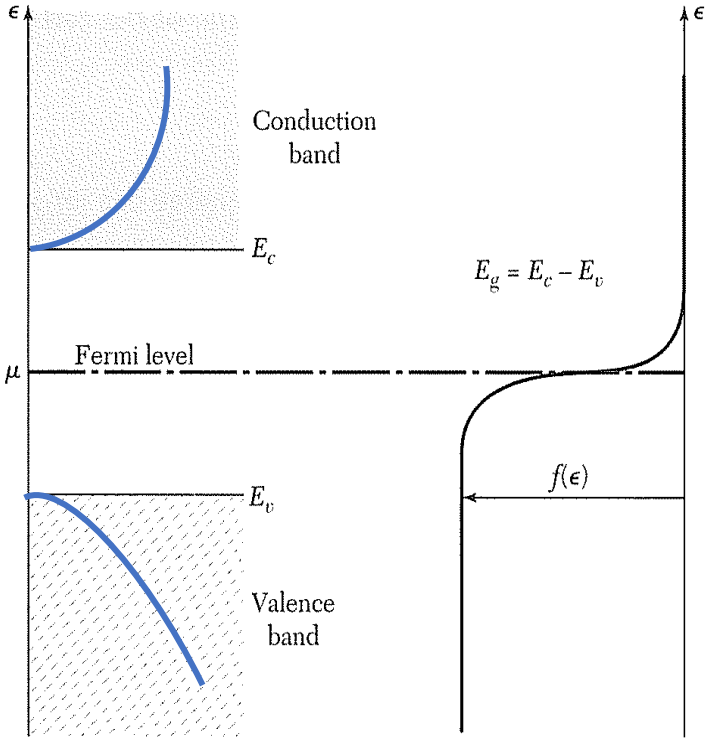


Metals, semimetals, semiconductors and insulators can be categorized by their carrier concentrations at room temperature. They can also be differentiated by the electrical resistivity at room temperature. Semiconductors usually have this value in the range of 10^{-2} to 10^{9} ohm-cm, and dependent on temperature strongly. At absolute zero a pure, perfect crystal of most semiconductors will be an insulator with a resistivity above 10^{14} ohm-cm.

Intrinsic Carrier Concentrations

For a semiconductor, we want to know the concentration of intrinsic carries as function of temperature T, in terms of its band gap E_g.

The energy of an electron in the conduction band is $\epsilon_k = E_c + \hbar^2 k^2 / 2m_e$



The density of electron states at ϵ is

$$D_e(\epsilon) = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}(\epsilon - E_c)^{1/2}$$

Fermi-Dirac distribution for $\epsilon - \mu >> k_B T$ reduces to

$$f_e \simeq \exp[(\mu - \epsilon)/k_B T] \ .$$

The concentration of electrons in the conduction band is

$$n = \int_{E_c}^{\infty} D_e(\epsilon) f_e(\epsilon) d\epsilon = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} \exp(\mu/k_B T) \times$$

$$\int_{E_c}^{\infty} (\epsilon - E_c)^{1/2} \exp(-\epsilon/k_B T) d\epsilon \ ,$$

which integrates to give

$$n = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} \exp[(\mu - E_c)/k_B T] \ .$$

Impurity Carrier Concentrations

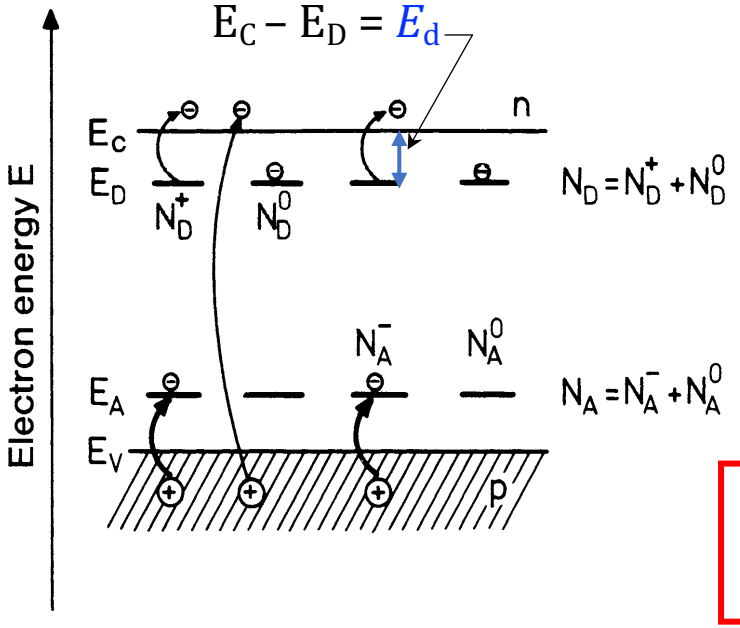
For a doped semiconductor, we want to know the concentration of conductive carries as function of temperature T and impurity energy levels E_d and E_a.

Neutrality condition demands $n + N_{\mathrm{A}}^{-} = p + N_{\mathrm{D}}^{+}$, in which

$$N_{\mathrm{D}} = N_{\mathrm{D}}^{0} + N_{\mathrm{D}}^{+} \,, \qquad N_{\mathrm{A}} = N_{\mathrm{A}}^{0} + N_{\mathrm{A}}^{-} \,.$$

and

$$n_{\mathrm{D}} = N_{\mathrm{D}}^{0} = N_{\mathrm{D}}[1 + \exp(E_{\mathrm{D}} - E_{\mathrm{F}})/\not{k}\, T]^{-1} \,,$$
$$p_{\mathrm{A}} = N_{\mathrm{A}}^{0} = N_{\mathrm{A}}[1 + \exp(E_{\mathrm{F}} - E_{\mathrm{A}})/\not{k}\, T]^{-1} \,.$$



For the case of a pure n-type semiconductor, with $N_D^+ >> n_i$,

$$n \approx N_{\mathrm{D}}^{+} = N_{\mathrm{D}} - N_{\mathrm{D}}^{0}$$
$$\approx N_{\mathrm{D}} \left(1 - \frac{1}{1 + \exp[(E_{\mathrm{D}} - E_{\mathrm{F}})/\not{k}\, T]} \right) .$$

Since $(n/N_{\mathrm{eff}}^{\mathrm{C}})\mathrm{e}^{E_{\mathrm{C}}/\not{k}\, T} = \mathrm{e}^{E_{\mathrm{F}}/\not{k}\, T}$,

$$n \approx \sqrt{N_{\mathrm{D}} N_{\mathrm{eff}}^{\mathrm{C}}}\, \mathrm{e}^{-E_{\mathrm{d}}/2\not{k}\, T}$$

The distribution function f_h for holes is related to the electron distribution function f_e by

$$f_h = 1 - \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1} = \frac{1}{\exp[(\mu - \epsilon)/k_B T] + 1}$$
$$\cong \exp[(\epsilon - \mu)/k_B T] \ , \quad \text{provided } (\mu - \epsilon) \gg k_B T.$$

The density of hole states at ϵ is

$$D_h(\epsilon) = \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2}(E_v - \epsilon)^{1/2}$$

The concentration p of holes in the valence band is

$$p = \int_{-\infty}^{E_v} D_h(\epsilon) f_h(\epsilon) d\epsilon = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} \exp[(E_v - \mu)/k_B T]$$

We multiply together the expressions for n and p to obtain the equilibrium relation

$$np = 4\left(\frac{k_B T}{2\pi\hbar^2}\right)^3 (m_e m_h)^{3/2} \exp(-E_g/k_B T), \qquad E_g = E_c - E_v$$

The product of np is constant at a given temperature.

For intrinsic carriers, n_i and p_i,

$$n_i = p_i = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} (m_e m_h)^{3/4} \exp(-E_g/2k_B T)$$

To obtain the Fermi level μ, we start from $n_i = p_i$, so

$$n_i = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} \exp[(\mu - E_c)/k_B T = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} \exp[(E_c - \mu)/k_B T] = p_i$$

then,

$$\exp(2\mu/k_B T) = (m_h/m_e)^{3/2} \exp(E_g/k_B T) \ ;$$

$$\mu = \tfrac{1}{2} E_g + \tfrac{3}{4} k_B T \ln (m_h/m_e) \ .$$

If $m_h = m_e$, then $\mu = \frac{1}{2} E_g$ and the Fermi level is in the middle of the gap.

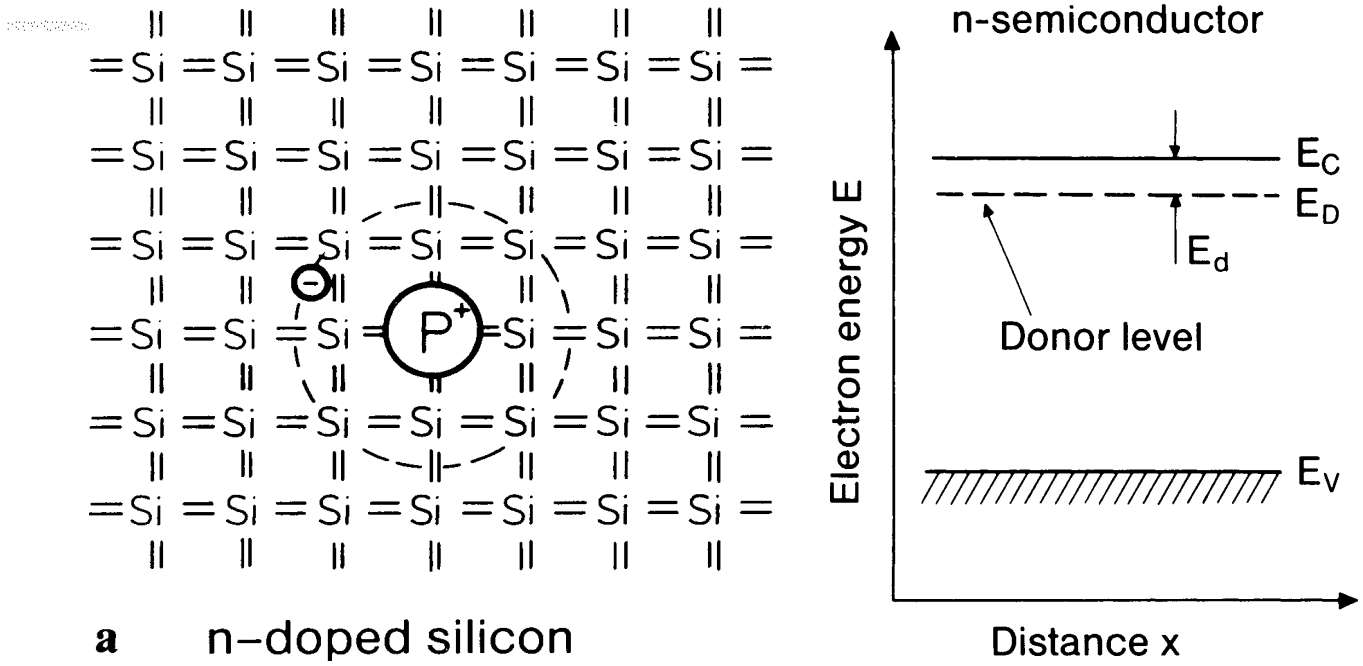
Impurity Conductivity

Certain impurities and imperfections drastically affect the electrical properties of a semiconductor. The addition of boron to silicon in the proportion of 1 boron atom to 10^5 silicon atoms increases the conductivity of pure at room temperature by a factor of 10^3. The deliberate addition of impurities to a semiconductor is called **doping**.

We consider the effect of impurities in silicon and germanium. These elements crystallize in the diamond structure. Each atom forms four covalent bonds, one with each of its nearest neighbors, corresponding to the chemical valence four. If an impurity atom of valence five, such as phosphorus, arsenic, or antimony, is substituted in the lattice in place of a normal atom, there will be one valence electron from the impurity atom left over after the four covalent bonds are established with the nearest neighbors, that is, after the impurity atom has been accommodated in the structure with as little disturbance as possible.

Donor States

The impurity atoms of valence five such as P, As, and Sb are called **donors** because they donate electrons to the conduction band in order to complete the covalent bonds with neighbor atoms, leaving electrons in the band.



a n–doped silicon

The extra electron moves in the coulomb potential $e/\epsilon r$ of the impurity ion, where ϵ in a covalent crystal is the static dielectric constant

We estimate the ionization energy of the donor impurity. The Bohr theory of the hydrogen atom may be modified to take into account the ϵ constant of the medium and the effective mass of an electron in the periodic potential of the crystal. The ionization energy of atomic hydrogen is $-e^4m/2\hbar^2$ In the semiconductor with dielectric constant ϵ we replace e^2 by e^2/ϵ and m by the effective mass m_e to obtain

$$E_d = \frac{e^4 m_e}{2\epsilon^2\hbar^2} = \left(\frac{13.6}{\epsilon^2}\frac{m_e}{m}\right) eV \; ; \qquad \text{and} \qquad a_d = \frac{\epsilon\hbar^2}{m_e e^2} = \left(\frac{0.53\epsilon}{m_e/m}\right) \text{Å}$$

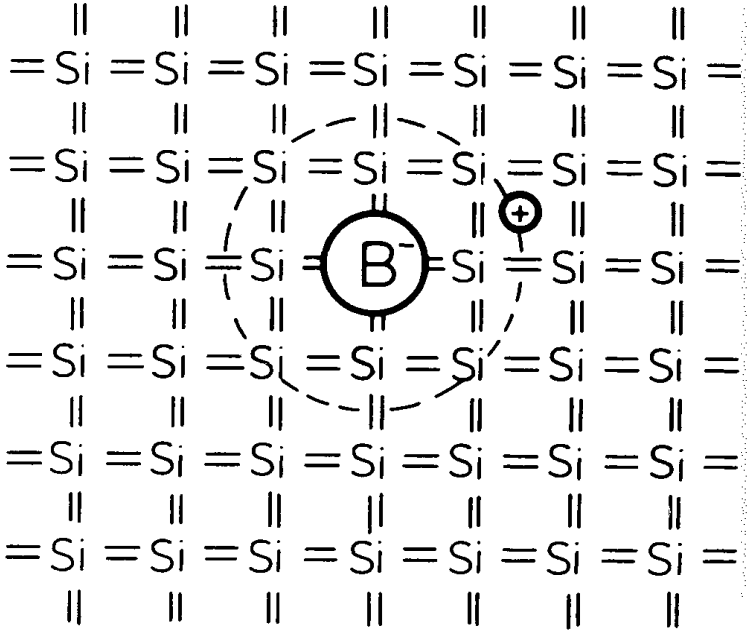
E_d is the ionization energy and a_d the Bohr radius of the donor.

To obtain a general impression of the impurity levels we use $m_e \approx 0.1\ m$ for electrons in germanium and $m_e \approx 0.2\ m$ in silicon. The static dielectric constant ϵ is 15.8 for Ge and 11.7 for Si. Then, we obtain

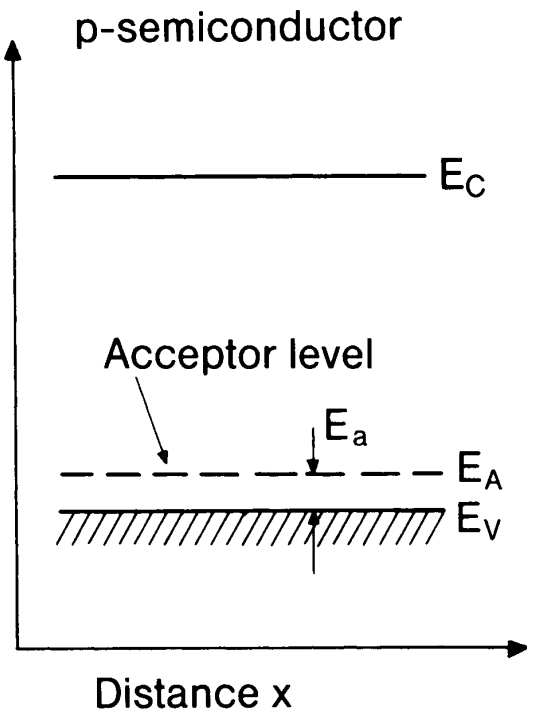
E_d = 5 meV and a_d = 80 Å for Ge;

E_d = 20 meV and a_d = 30 Å for Si.

Acceptor States



b p-doped silicon



Trivalent impurities such as B, Al, Ga, and In are called **acceptors** because they accept electrons from the valence band in order to complete the covalent bonds with neighbor atoms, leaving holes in the band.

Carrier Mobility

The mobility is the magnitude of the drift velocity of a charge carrier per unit electric field: $\mu = |v|/E$

The electrical conductivity is the sum of the electron and hole contributions:

$$\sigma = (ne\mu_e + pe\mu_h),$$

The drift velocity of a charge q was found to be $v = q\tau E/m$, whence

$\mu_e = e\tau_e/m_e$; $\mu_h = e\tau_h/m_h$, where τ is the collision time.

Table 3 Carrier mobilities at room temperature, in $cm^2/V\text{-}s$

Crystal	Electrons	Holes	Crystal	Electrons	Holes
Diamond	1800	1200	GaAs	8000	300
Si	1350	480	GaSb	5000	1000
Ge	3600	1800	PbS	550	600
InSb	800	450	PbSe	1020	930
InAs	30000	450	PbTe	2500	1000
InP	4500	100	AgCl	50	—
AlAs	280	—	KBr (100 K)	100	—
AlSb	900	400	SiC	100	10–20

Thermoelectric Effect

The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa via a thermocouple. The term "thermoelectric effect" encompasses three separately identified effects: the Seebeck effect, Peltier effect, and Thomson effect. The Seebeck and Peltier effects are different manifestations of the same physical process; textbooks may refer to this process as the Peltier–Seebeck effect.

The charge flux is, assuming only electrons involved,

$$j_q = n(-e)(-\mu_e)E = ne\mu_e E \quad , \text{ where } \mu_e \text{ is the electron mobility.}$$

Then the energy flux due to the electrons is

$$j_U = n(E_c - \mu + \tfrac{3}{2}k_B T)(-\mu_e)E$$

each electron carries energy $(E_c - \mu) + \tfrac{3}{2}k_B T$

The **Peltier coefficient** Π is defined by $j_U = \Pi j_q$, so

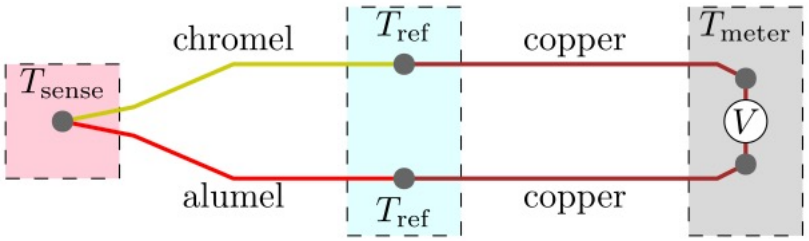
$$\Pi_e = -(E_c - \mu + \tfrac{3}{2}k_B T)/e \,, \qquad \text{for electrons}$$

$$\Pi_h = (\mu - E_v + \tfrac{3}{2}k_B T)/e \quad , \qquad \text{for holes}$$

Applications of Thermoelectric Effect

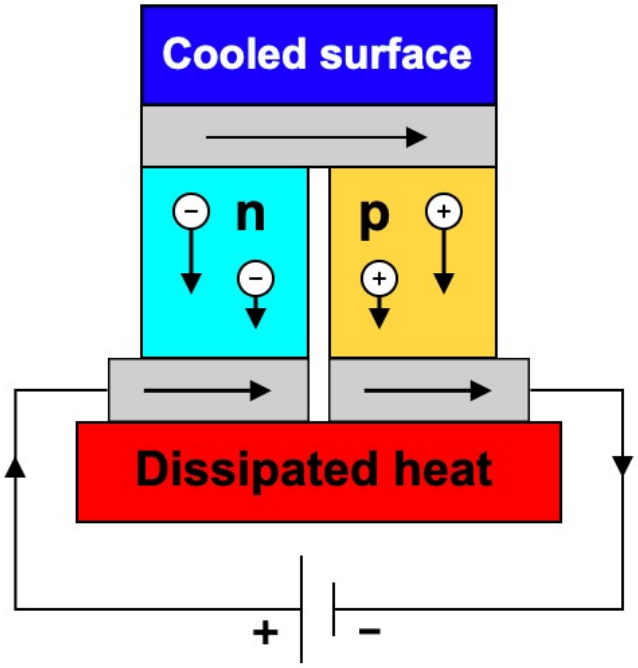
$$\mathbf{E}_{\text{emf}} = -S\nabla T,$$

where *S* is the Seebeck coefficient (also known as thermopower).



temperature-sensing thermocouple

K-type thermocouple (chromel-alumel) in the standard thermocouple measurement configuration. The measured voltage *V* can be used to calculate temperature T_{sense}, provided that temperature T_{ref} is known.



thermoelectric cooler

Bloch oscillations

The one-dimensional equation of motion for an electron with wave vector k in a constant electric field E is:

$$\frac{dp}{dt} = \hbar\frac{dk}{dt} = -eE, \qquad \Rightarrow \qquad k(t) = k(0) - \frac{eE}{\hbar}t.$$

Suppose the dispersion relation for a given band is $\mathcal{E}(k) = A\cos ak,$

The group velocity v of the electron is given by

$$v(k) = \frac{1}{\hbar}\frac{d\mathcal{E}}{dk} = -\frac{Aa}{\hbar}\sin ak\,,$$

and the electron position x can be computed as a function of time:

$$x(t) = \int_0^t v(k(t'))dt' = x(0) + \frac{A}{eE}\cos\left(\frac{aeE}{\hbar}t\right).$$

This shows that the electron oscillates in real space. The angular frequency of the oscillations is given by

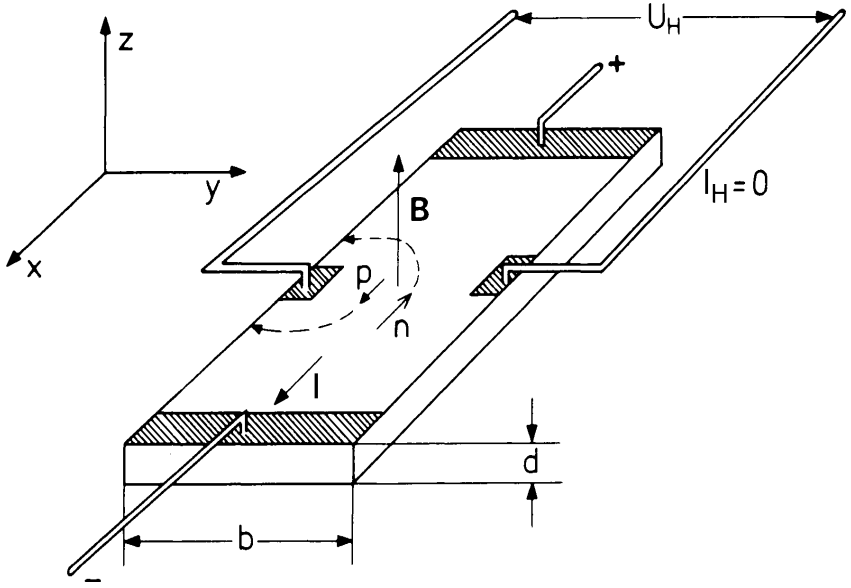
$$\omega_B = ae|E|/\hbar.$$

Bloch oscillations are not routinely observed because the electrons in a periodic system undergo collisions with ions in the lattice much too frequently, on the time scale of τ ($\approx 10^{-14}$ s).

Hall Effect

To separately determine the carrier concentration n and the mobility μ appearing in the conductivity $\sigma = ne\mu$, one measures both the conductivity and the Hall effect. The Lorentz force on an electron moving in the x direction with velocity v_x is:

$$F_y = -e(v \times \boldsymbol{B})_y - e\mathscr{E}_y = ev_xB - e\mathscr{E}_y = 0 \ .$$



Assuming that the current is carried exclusively by electrons, we have

$$j_x = I/(b\,d) = -n\,e\,v_x$$

and

$$\mathscr{E}_y = \frac{U_\mathrm{H}}{b} = -\frac{1}{n\,e} j_x B = -\frac{1}{n\,e}\frac{IB}{bd} \ .$$

$$U_\mathrm{H} = R_\mathrm{H} I\,B/d \ , \quad R_\mathrm{H} = -(ne)^{-1}.$$

The sign of R_H gives the type of carrier.

Problems

1. ***Impurity orbits.*** Indium antimonide has $E_g = 0.23$ eV; dielectric constant $\epsilon = 18$; electron effective mass $m_e = 0.015\ m$. Calculate (a) the donor ionization energy; (b) the radius of the ground state orbit. (c) At what minimum donor concentration will appreciable overlap effects between the orbits of adjacent impurity atoms occur? This overlap tends to produce an impurity band—a band of energy levels which permit conductivity presumably by a hopping mechanism in which electrons move from one impurity site to a neighboring ionized impurity site.

2. ***Hall effect with two carrier types.*** Assuming concentration n, p; relaxation times τ_e, τ_h; and masses m_e, m_h, show that the Hall coefficient in the drift velocity approximation is

(CGS)
$$R_H = \frac{1}{ec} \cdot \frac{p - nb^2}{(p + nb)^2},$$

where $b = \mu_e/\mu_h$ is the mobility ratio. In the derivation neglect terms of order B^2. In SI we drop the c. Hint: In the presence of a longitudinal electric field, find the transverse electric field such that the transverse current vanishes. The algebra may seem tedious, but the result is worth the trouble. Use (6.64), but for two carrier types; neglect $(\omega_c\tau)^2$ in comparison with $\omega_c\tau$.

3. A semiconductor with a band gap energy E_g of 1eV and equal hole and electron effective masses $m_e^* = m_h^* = m_0$ (m_0 is free electron mass) is p-doped with an acceptor concentration of $p = 10^{-18}$ cm^{-3}. The acceptor energy level is located 0.2 eV above the valence band edge of the material.

a) Show that intrinsic conduction in this material is negligible at 300 K.

b) Calculate the conductivity σ of the material at room temperature (300 K), given a hole mobility of $\mu_p = 100$ cm^2/Vs at 300 K.

c) Plot the logarithm of the hole concentration, ln p, versus reciprocal temperature 1/T for the temperature range 100 to 1000 K.